

## Rutin Content of *Sophora japonica* L.

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Unopened flower buds of the Chinese Scholar tree are used for medicinal purposes in China under the name "Wai Fa," the "blossom of the tree." This material contains four to five times as much rutin as does buckwheat, our best domestic source of that glycoside. Specimens were collected from a tree near this Laboratory throughout the growing season. As the buds opened into flowers, the rutin content declined, and continued to decrease as the seed pods formed. When the seeds were in the soft green stage, the seed pods contained no rutin. Rutin in small quantities was isolated from the leaflets of the tree.

In 1853 Stein<sup>2</sup> isolated rutin from a commercial dyeing material known as "Chinese yellow berries" but of unknown botanical origin. He purified the pigment and identified it with "rutinic acid," discovered in garden rue by Weiss<sup>3a</sup> in 1842 and isolated from capers by Rochleder and Hlasiwetz.<sup>3b</sup> Martius<sup>4</sup> identified the "berries" as the unopened flower buds of *Sophora japonica* L., known in China as "Wai Fa" and used for centuries in Chinese medicine for hemorrhagic and other diseases much as rutin is now being used in western medicine. Common names for the tree are Japanese pagoda tree and Chinese Scholar tree.

Early supplies of rutin for pharmaceutical manufacturing were obtained from the leaves and blossoms of buckwheat.<sup>5</sup> Other sources, such as pansy petals, are much richer in rutin but not practicable. At first, sophora did not appear to be a promising material. None of it could be located in this country, and preliminary information from China indicated that no adequate supply could be expected from that quarter. Samples were obtained from Shanghai, through Dr. T. T. Pan, the analysis of which indicated a rutin content of 16.8% on a dry basis, that is, four to five times the rutin content of commercial buckwheat leaf meals. Evidently such a material would be of economic importance if sufficient could be obtained to satisfy manufacturing demands.

In 1947, a report was received that 10 tons of

\* Deceased.

(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(2) W. Stein, *J. prakt. Chem.*, **58**, 399 (1853).

(3) (a) A. Weiss, *Pharm. Centr.*, **13** (II) 903 (1842); (b) Rochleder and Hlasiwetz, *Ann. Chem. Pharm.*, **82**, 197 (1852).

(4) Martius, *Arch. Pharm.*, **160**, 231 (1862).

(5) J. F. Couch, C. F. Krewson, J. Naghski and M. J. Copley, U. S. Dept. Agr., Bur. Agr. Ind. Chem., BRRL, AIC 115, 1946 (Processed).

sophora had been imported into New York and was being offered for sale. A sample of this shipment contained 12.8% of rutin. The point of origin of this sophora was not revealed, but it may have been Hong Kong. Since then, shipments of sophora have arrived at intervals, and supplies are said to be plentiful. Samples of seven lots have been examined. They averaged 16.3% of rutin (dry basis), identified by chemical and spectrophotometric methods, with a maximum of 19.7 and a minimum of 12.8%. At present, sophora has displaced buckwheat as the source-material in rutin manufacture.

The sophora tree grows in northern China, being common around Peiping, in Korea and in parts of Japan. Japanese rutin manufacturers, however, import their sophora from China.<sup>6</sup> The tree is grown as an ornamental in the United States, being fairly common in some localities. Material for the present investigation was collected from a splendid specimen growing in the Morris Arboretum of the University of Pennsylvania, through the courtesy of Henry T. Skinner, Curator of the botanical garden.

### Experimental

Flowering heads were collected at intervals throughout the growing season, beginning with the unopened flower buds and continuing as these developed into flowers and then formed seed pods. Part of the green material was immediately analyzed for rutin content. Other portions were used for moisture determination, or were dried either in air or at 110° in an electric oven.

Results of analyses of the green material are presented in Table I. The rapid drop in rutin content as the buds unfolded into bloom is consistent with similar behavior in buckwheat,<sup>7</sup> hydrangea<sup>8</sup> and pansies. The complete disappearance of rutin in the seed pods, whether young or

(6) Tatsuo Keimatsu, Kyoto, personal communication.

(7) J. F. Couch, J. Naghski and C. F. Krewson, *Science*, **103**, 197 (1946).

(8) J. F. Couch and J. Naghski, *This Journal*, **87**, 1419 (1945).

mature, is similar to the case of buckwheat seed, which contains no rutin. Indeed, rutin appears to be associated with actively metabolizing tissues, and therefore, must play an important role in plant physiology.

TABLE I

ROUTIN CONTENT OF FRESH SOPHORA			
Date collected 1947	Part of plant	Moisture, %	Rutin content, % (mfb.)
July 15	Panicle with unopened buds	69.0	22.9
July 22	Panicle; a few opened buds	72.7	22.5
Aug. 5	Panicle; one-half of flowers in full bloom	71.7	17.6
Sept. 18	Green seed pods	74.7	None
Nov. 6	Mature seed pods	41.0	None
Dec. 15	Mature seed pods	21.4	None
Sept. 18	Pedicels and flower stalks	61.7	4.6
Nov. 6	Pedicels	56.3	1.5
Dec. 15	Pedicels	43.2	3.7

The rutin content of the pedicels, however, persisted through the season. These flower stalks continued alive while the seed pods were maturing, which may account for this fact. Three collections of leaflets were made during the season. A test for flavonols was positive. On analysis, amorphous deposits unlike crystalline rutin were obtained. Chromatographic analyses on paper<sup>9,10</sup> separated these into three fractions, two of which could readily be identified as rutin and quercetin, respectively. The third fraction unidentified, may be one of the minor glycosides reported by Zemlén and Bognár<sup>11</sup> or Charaux and Rabaté.<sup>12</sup> Approximate values for these constituents were obtained by estimating the size and intensity of the spots in comparison with known quantities of rutin and quercetin. The data are presented in Table II.

(9) S. H. Wender and T. B. Gage, *Science*, **109**, 287 (1949).

(10) E. C. Bate-Smith and R. G. Westall, *Biochim. et Biophys. Acta*, **4**, 427 (1950).

(11) G. Zemlén and R. Bognár, *Ber.*, **75B**, 482 (1942).

(12) C. Charaux and J. Rabaté, *Bull. soc. chim. biol.*, **20**, 454 (1938).

TABLE II

RESULTS OF CHROMATOGRAPHIC ANALYSIS OF FLAVONOL FRACTIONS FROM SOPHORA LEAFLETS AND SEED PODS

Sample	Part of plant	Crude flavonols, %	Chromatographic results, %		
			Rutin $R_F = 0.05$	Flavonol $R_F = 0.17$	Quercetin $R_F = 0.90$
47-177	Seed pods	1.5	0.75	0.75	..
47-178	Leaflets	0.4	.2	..	0.2
47-204	Leaflets	0.2	.2	..	0.02
47-205	Seed pods	1.0	.5	0.5	..
47-211	Seed pods	0.4	.2	0.2	..
48-14	Leaflets	4.3	4.1	Trace	Trace
48-16	Woody twigs	0.4	0.4	..	..

\* The approximate values reported under the chromatographic analysis are based on an estimate of the size of the spots. In most cases, the rutin spot and spot of the flavonol with  $R_F$  0.17 were about the same size and intensity.

When dried, either in air or by heat, sophora behaved like other rutin bearing plants,<sup>7</sup> that is, there was a variable but appreciable loss of rutin during the process, as shown in Table III. In two of the three pairs of experiments, the air-dried sophora appeared to contain slightly more rutin. Considering the difficulties of sampling and the errors in analysis, these differences are not thought to be significant.

TABLE III

EFFECT OF DRYING ON ROUTIN CONTENT OF SOPHORA

Date collected 1947	Conditions of drying	Rutin content, %		Loss of rutin
		Before drying	After drying	
July 15	Oven-dried at 110°	22.9	17.9	21.8
July 22	Oven-dried at 110°	22.5	15.7	30.2
July 22	Air-dried	22.5	16.0	28.9
Aug. 5	Oven-dried at 110°	17.6	13.2	25.0
Aug. 5	Air-dried	17.6	15.9	9.7
Aug. 18	Oven-dried at 110°	20.2	16.3	19.3
Aug. 18	Air-dried	20.2	13.3	34.2